

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : AISIN SEIKI CO LTD

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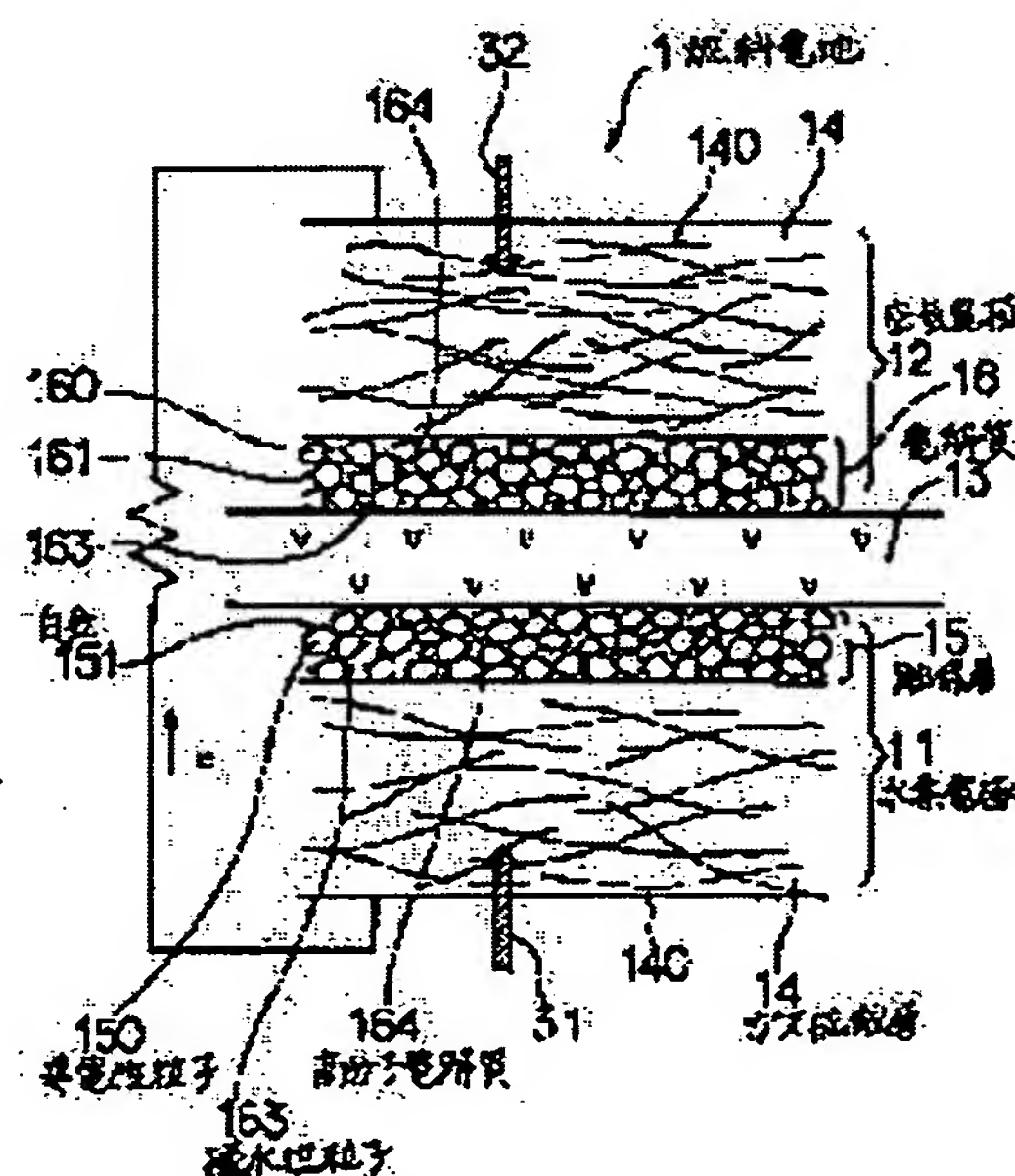
MATSUOKA AKIRA

## (54) AIR ELECTRODE FOR FUEL CELL AND MANUFACTURE THEREOF

(57)Abstract:

**PROBLEM TO BE SOLVED:** To improve the air utilization factor by forming an electrode of a gas diffused layer and catalyst layers formed on the surface of the gas diffused layer, and forming the catalyst layer of conductive grains, water repellent grains, high molecular electrolyte, main catalyst and auxiliary catalyst.

**SOLUTION:** A hydrogen electrode 11 and an air electrode 12 of a fuel cell 1 are respectively formed of a gas diffused layer 14 and catalyst layers 15, 16 formed on the surface of the gas diffused layer. The catalyst layer 16 of the air electrode 12 is formed of carbon black as conductive grains 160, PTFE as water repellent grains 163, positive ion exchange resin as high molecular electrolyte 164, granular platinum as main catalyst 161 and vanadium oxide as auxiliary catalyst 162. The catalyst layer 15 of the hydrogen electrode 11 is formed of carbon black as conductive grains 160, granular platinum carried by the carbon black, PTFE as water repellent grains 163 and positive ion exchange resin as high molecular electrolyte 164. The gas diffused layer 14 of the electrodes 11, 12 is formed of a carbon fiber plate formed by laminating carbon fibers 140.



## LEGAL STATUS

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| [Date of request for examination]   | 01.07.2003 |
| [Date of sending the examiner's decision of rejection]  |            |
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CLAIMS

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[Claim(s)]

[Claim 1] It is the air electrode for fuel cells characterized by being the air electrode for fuel cells which consists of a gaseous diffusion layer and a catalyst bed formed in the front face, for the above-mentioned catalyst bed consisting of a conductive particle, a water-repellent particle, a polyelectrolyte, a main catalyst, and a co-catalyst, and this co-catalyst consisting of a vanadium oxide, cerium oxide, a zirconium dioxide, or two or more sorts of complex of these matter.

[Claim 2] It consists of a gaseous diffusion layer and a catalyst bed formed in the front face. This catalyst bed It consists of a conductive particle, a water-repellent particle, a polyelectrolyte, a main catalyst, and a co-catalyst. Moreover, this co-catalyst A vanadium oxide, cerium oxide, a zirconium dioxide In manufacturing the air electrode for fuel cells which consists of two or more sorts of complex of these matter, platinum is supported in the conductive particle layer which constitutes the above-mentioned catalyst bed. Subsequently this conductive particle layer or at least one of vanadium, a cerium, and the zirconiums The manufacture approach of the air electrode for fuel cells which immerses and dries in the solution to contain and is characterized by the thing [ carrying out afterbaking ].

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the air electrode and its manufacture approach of the fuel cell which consists of a hydrogen electrode, an air electrode, and an electrolyte arranged among both.

[0002]

[Description of the Prior Art] Conventionally, as shown in below-mentioned drawing 1, it consists of a hydrogen electrode 11, an air electrode 12, and an electrolyte 13 arranged among both, and the fuel cell 1 which uses hydrogen and oxygen as an electrode active material is known. In the above-mentioned fuel cell 1, both the hydrogen electrode 11 and the air electrode 12 consist of a gaseous diffusion layer 14 and catalyst beds 15 and 16 formed in the front face, and these catalyst beds 15 and 16 consist of carbon black which is the conductive particle 150, 160, and the platinum particles 151 and 161 supported by this, the water-repellent particle 163 and a polyelectrolyte 164.

[0003] Generating of the electromotive force in the above-mentioned fuel cell is performed as shown below. The air as oxygen content gas is supplied for hydrogen content gas to the above-mentioned hydrogen electrode from the exterior at an air electrode. Thereby, the electrode reaction  $O(1/2)2+2e^-+2H^+ \rightarrow H_2O$  occurs in  $H_2 \rightarrow 2H^++2e^-$  and an air electrode with a hydrogen electrode. Therefore, the cell reaction  $H_2+(1/2)O_2 \rightarrow H_2O$  occurs, and, thereby, a fuel cell carries out electromotive. And the platinum particle which exists in the above-mentioned catalyst bed is bearing the catalysis in this electrode reaction.

[0004]

[Problem(s) to be Solved] By the way, the cell engine performance in the fuel cell of the above-mentioned structure is governed by the polarization property of an air electrode, therefore its improvement in the property of a near catalyst bed of an air electrode is effective for improvement in the cell engine performance.

[0005] That is, the above-mentioned conventional fuel cell had the low air utilization rate supplied to the air electrode, therefore the air content needed to be made [ many ] for improvement in the cell engine performance. It is possible to make large-sized the compressor used as a remedy to this problem, for example in order to send air into a fuel cell. However, when using the above-mentioned fuel cell in the condition of having been restricted to installation tooth spaces, such as an electric vehicle, it is difficult to use a large-sized compressor. Therefore, an air utilization rate is raised and the fuel cell which can obtain electrical potential difference sufficient also with a small amount of air is demanded.

[0006] This invention tends to offer the air electrode for fuel cells which can raise an air utilization rate, and its manufacture approach in view of this trouble.

[0007]

[Means for Solving the Problem] Invention of claim 1 is an air electrode for fuel cells which consists of a gaseous diffusion layer and a catalyst bed formed in the front face, the above-mentioned catalyst bed consists of a conductive particle, a water-repellent particle, a polyelectrolyte, a main catalyst, and a co-catalyst, and this co-catalyst is in the air electrode for fuel cells characterized by consisting of a vanadium oxide, cerium oxide, a zirconium dioxide, or two or more sorts of complex of these matter.



[0008] As a fuel cell which prepares the above-mentioned air electrode for fuel cells, as shown in below-mentioned drawing 1, it consists of a hydrogen electrode, an air electrode, and an electrolyte arranged among both, and the fuel cell which uses hydrogen and oxygen as an electrode active material can be mentioned, for example. To the above-mentioned air electrode, air can be supplied through a gaseous diffusion layer from the exterior, and the electrode reaction which consumed and mentioned above the oxygen contained in this occurs. In addition, supply of the above-mentioned air can use an air compressor, and can be performed by sending in the open air to an air electrode as it is.

[0009] Moreover, as the above-mentioned gaseous diffusion layer, the carbon fiber plate which accumulated the carbon fiber and was fabricated can be used, for example. As the above-mentioned conductive particle, cation exchange resin can be used as carbon black and the above-mentioned water-repellent particle, for example, for example as polytetrafluoroethylene (it abbreviates to PTFE henceforth), and the above-mentioned polyelectrolyte.

[0010] The above-mentioned main catalyst has the role which promotes electrode reaction in the above-mentioned air electrode, for example, platinum can be used for it. Moreover, the amount of support of the co-catalyst in the above-mentioned catalyst bed is 0.1 - 2.0 mg/cm<sup>2</sup>. Carrying out is desirable. The amount of support of the above-mentioned co-catalyst is 2.0 mg/cm<sup>2</sup>. In many, it becomes the structure which prevents a gas passageway conversely, electric resistance is increased further, and there is a possibility of causing the fall of a property. On the other hand, it is 0.1 mg/cm<sup>2</sup>. In being the following, there is a possibility that the function as a co-catalyst may not fully work. In addition, the unit "mg/cm<sup>2</sup>" of the amount of support of the above-mentioned co-catalyst means the weight of the co-catalyst supported by per unit area of an electrode.

[0011] Moreover, as for the amount of support of the water-repellent particle in the above-mentioned catalyst bed, it is desirable to be referred to as conductive particle:water repellence particle = 8:2-6:4 (weight ratio). When the amount of support of the above-mentioned water-repellent particle is less than 8:2, there is fear that water repellence is weak. On the other hand, in [ than 6:4 ] more, there is a possibility that electric resistance may become large. In addition, the most desirable amount of support of the above-mentioned water-repellent particle is conductive particle:water repellence particle = 7:3 (weight ratio).

[0012] Moreover, as for the amount of support of the polyelectrolyte in the above-mentioned catalyst bed, it is desirable to consider as 0.08 - 2 mg/cm<sup>2</sup>. The amount of support of the above-mentioned polyelectrolyte is 0.08 mg/cm<sup>2</sup>. In being the following, there is a possibility that electrode reaction may become late. On the other hand, it is 2 mg/cm<sup>2</sup>. In many, there is a possibility that electric resistance may become large. In addition, the amount of support of the above-mentioned polyelectrolyte is dry weight, and the unit is the same as the case of the above-mentioned co-catalyst.

[0013] It explains below about an operation of this invention. In the catalyst bed concerning this invention, a vanadium oxide, cerium oxide, a zirconium dioxide, or two or more sorts of complex of these matter are supported as a co-catalyst. These matter is oxides with the unfixed number of the oxygen atom combined to vanadium, a cerium, and zirconium 1 atom. And drawing 3 which mentions the above-mentioned matter later, and the oxygen atom which shows drawing 4 and which untied, has chain-like structure and was combined with the specific part can go in and out comparatively freely (the oxygen atom concerning the A section enclosed by the dotted line in this drawing corresponds).

[0014] Therefore, the above-mentioned matter can emit an oxygen atom, if a surrounding ambient atmosphere serves as oxygen Lean, and if a surrounding ambient atmosphere serves as oxygen Rich on the other hand, it can absorb an oxygen atom. Therefore, in near [ above-mentioned ] a catalyst bed, oxygen can always be held to the concentration more than fixed. Therefore, in an air electrode, an overvoltage can be stopped low and an air utilization rate can be raised. Moreover, since oxygen is emitted from the above-mentioned co-catalyst when supply of air runs short temporarily, an air electrode can continue electrode reaction using this emission oxygen.

[0015] As mentioned above, according to this invention, the air electrode for fuel cells which can raise an air utilization rate can be offered.

[0016] Invention of claim 2 consists of a gaseous diffusion layer and a catalyst bed formed in the

front face. Next, this catalyst bed It consists of a conductive particle, a water-repellent particle, a polyelectrolyte, a main catalyst, and a co-catalyst. Moreover, this co-catalyst A vanadium oxide, cerium oxide, a zirconium dioxide In manufacturing the air electrode for fuel cells which consists of two or more sorts of complex of these matter, platinum is supported in the conductive particle layer which constitutes the above-mentioned catalyst bed. Subsequently this conductive particle layer or at least one of vanadium, a cerium, and the zirconiums It immerses and dries in the solution to contain and is in the manufacture approach of the air electrode for fuel cells characterized by the thing [ carrying out afterbaking ].

[0017] Thereby, it is the air electrode using platinum as a main catalyst, and the air electrode for fuel cells which can raise the air utilization rate in a fuel cell shown in claim 1 can be obtained.

Moreover, it is desirable to perform previously the platinum which serves as a main catalyst to a conductive particle in the above-mentioned manufacture approach on the occasion of support and support of a co-catalyst on the conditions of the heat treatment temperature of 350 degrees C or less. Thereby, condensation of platinum can be prevented.

[0018] Moreover, as a solution containing at least one of the above-mentioned vanadium, a cerium, and the zirconiums, the ethanol solution of perchloric acid vanadium, the ethanol solution of a cerium nitrate, the ethanol solution of zirconium nitrate, etc. can be mentioned, for example.

[0019]

[Embodiment of the Invention]

It explains using drawing 1 and drawing 2 about the fuel cell which prepared the air electrode for fuel cells concerning the example of an operation gestalt of example of operation gestalt 1 this invention, and this electrode. As shown in drawing 1 and drawing 2 , the air electrode 12 for fuel cells of this example consists of a gaseous diffusion layer 14 and a catalyst bed 16 formed in the front face, the above-mentioned catalyst bed 16 consists of the conductive particle 160, the water-repellent particle 163, a polyelectrolyte 164, a main catalyst 161, and a co-catalyst 162, and this co-catalyst 162 consists of a vanadium oxide.

[0020] First, it explains per [ concerning this example ] fuel cell 1. As shown in drawing 1 , the above-mentioned fuel cell 1 is a fuel cell which consists of a hydrogen electrode 11, an air electrode 12, and a solid electrolyte 13 arranged among both, and uses hydrogen and oxygen as an electrode active material. In the above-mentioned fuel cell 1, both the hydrogen electrode 11 and the air electrode 12 consist of a gaseous diffusion layer 14 and catalyst beds 15 and 16 formed in the front face.

[0021] And the catalyst bed 16 of the above-mentioned air electrode 12 consists of a vanadium oxide which is particle-like the platinum and the co-catalyst 162 which are the cation exchange resin which is PTFE and the polyelectrolyte 164 which are the carbon black which is the conductive particle 160, and the water-repellent particle 163, and the main catalyst 161 supported by the front face of the above-mentioned carbon black. Moreover, the catalyst bed 15 of the above-mentioned hydrogen electrode 11 consists of carbon black which is the conductive particle 150, and cation exchange resin which is PTFE and the polyelectrolyte 164 which are the platinum 151 of the shape of a particle supported by this, and the water-repellent particle 163.

[0022] Moreover, the gaseous diffusion layer 14 in the above-mentioned hydrogen electrode 11 and the air electrode 12 consists of a carbon fiber plate which accumulated the carbon fiber 140 and was fabricated. in addition, the amount of support to the catalyst bed 15 of the platinum 151 in the above-mentioned hydrogen electrode 11 -- 0.2 mg/cm<sup>2</sup> it is . the amount of support to the catalyst bed 16 of platinum [ in / on the other hand / the above-mentioned air electrode 12 ] 161 -- 0.2 mg/cm<sup>2</sup> it is .

[0023] moreover, the above-mentioned hydrogen electrode 11 and the above-mentioned air electrode 12 -- setting -- both -- the amount of support of the above-mentioned water-repellent particle 163 -- the amount of support of conductive particle:water repellence particle =7:3 (weight ratio) and the above-mentioned cation exchange resin 164 -- 0.4 mg/cm<sup>2</sup> it is .

[0024] And hydrogen content gas 31 is supplied to the above-mentioned hydrogen electrode 11, and air 32 is supplied to the air electrode 12. These hydrogen content gas 31 and air 32 are introduced from the gaseous diffusion layer 14 side in each electrode. Furthermore, between the above-mentioned hydrogen electrode 11 and the air electrode 12, the solid electrolyte 13 which consists of cation-exchange-resin film is arranged.



[0025] It explains per [ which is the co-catalyst of this example ] vanadium oxide. the above-mentioned vanadium oxide is shown in drawing 3 -- the time -- the shape of a chain -- it has structure. And the oxygen atom concerning the A section enclosed by the dotted line in this drawing goes in and out according to an external oxygen density.

[0026] Next, it explains per manufacture approach of the above-mentioned air electrode 12. First, by kneading the mixed powder of carbon black and PTFE with the solvent containing a binder to the above-mentioned gaseous diffusion layer 14, it is made the shape of a paste, a doctor blade is used on the above-mentioned gaseous diffusion layer 14, and it fabricates in the shape of a sheet.

[0027] Next, it is Pt (NO<sub>3</sub>) (NH<sub>3</sub>)<sub>2</sub> to the carbon black which carried out [ above-mentioned ] adhesion. A nitric-acid solution is heat-treated after sinking in and desiccation in the temperature of 180-300 degrees C, and a hydrogen gas ambient atmosphere (hydrogen reduction ambient atmosphere). By the above, particle-like platinum deposits on the front face of the above-mentioned carbon black. Next, to the above-mentioned carbon black, it sinks in and the ethanol solution of perchloric acid vanadium (VCl<sub>3</sub> O) is dried. Then, it heat-treats in the temperature of 350 degrees C, and air. Furthermore, it sinks into the above-mentioned catalyst bed 16, and it is made to dry a cation-exchange-resin solution. The air electrode 12 was obtained by the above.

[0028] Next, it explains per [ in this example ] operation effectiveness. In the catalyst bed 16 of the air electrode 12 of this example, as a co-catalyst 162, whenever it is shown in drawing 3 , it comes, and the vanadium oxide is supported. The above-mentioned vanadium oxide can emit an oxygen atom, if a surrounding ambient atmosphere serves as oxygen Lean, and if a surrounding ambient atmosphere serves as oxygen Rich on the other hand, it can absorb an oxygen atom. Therefore, in near [ catalyst bed 16 ] the above, the concentration of oxygen can always be held more than fixed.

[0029] Therefore, in the air electrode 12, an overvoltage can be stopped low, and an air utilization rate can be raised. Moreover, since oxygen is emitted from the above-mentioned co-catalyst 162 when supply of air runs short temporarily, the air electrode 12 can continue electrode reaction using this emission oxygen.

[0030] As mentioned above, according to this example, the air electrode for fuel cells which can raise an air utilization rate can be offered.

[0031] The example of two examples of an operation gestalt is the air electrode which used the Seria zirconia as a co-catalyst, as shown in drawing 4 . The air electrode concerning this example consists of a gaseous diffusion layer and a catalyst bed formed in the front face like the example 1 of an operation gestalt, and the above-mentioned catalyst bed consists of PTFE of carbon black and a water-repellent particle, cation exchange resin of a polyelectrolyte, and the platinum and the co-catalyst of a main catalyst that are a conductive particle.

[0032] And as shown in drawing 4 , the above-mentioned co-catalyst consists of Seria zirconia complex which has chain-like structure, and the oxygen atom concerning the A section enclosed by the dotted line in this drawing goes in and out according to an external oxygen density. Moreover, the chemical formula of the above-mentioned Seria zirconia complex is expressed with Ce<sub>1-X</sub> ZrX O<sub>2</sub> (x=0.4-0.7). Others are the same as that of the example 1 of an operation gestalt.

[0033] Next, it explains per manufacture approach of the air electrode of this example. The mixed powder of carbon black and PTFE is made to adhere to the gaseous diffusion layer which consists of a carbon fiber like the example 1 of an operation gestalt. Subsequently, platinum is made to support to the above-mentioned carbon black.

[0034] Next, to the above-mentioned carbon black, it sinks in and the ethanol solution of a cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub> and 6H<sub>2</sub> O) and the ethanol solution of zirconium nitrate (ZrO(NO<sub>3</sub>)<sub>2</sub> and 2H<sub>2</sub> O) are dried. Then, it heat-treats in the temperature of 350 degrees C, and air. Furthermore, it sinks into the above-mentioned catalyst bed, and it is made to dry a cation-exchange-resin solution. The air electrode was obtained by the above. In addition, also in the air electrode of this example, it has the same operation effectiveness as the example 1 of an operation gestalt.

[0035] The example of three examples of an operation gestalt explains the engine performance of the air electrode concerning this invention using the comparison sample C1 with a sample 1 and a sample 2. A sample 1 is the air electrode shown in the example 1 of an operation gestalt. A sample 2 is the air electrode shown in the example 2 of an operation gestalt. The comparison sample C1 is the same air electrode as the above-mentioned samples 1 and 2 except for not containing the co-catalyst.

[0036] In addition, the thickness also of the gaseous diffusion layer in which air electrode of the above-mentioned samples 1 and 2 and the comparison sample C1 is 180 micrometers, and the thickness of a catalyst bed is 20 micrometers. And the carbon black concerning the above-mentioned catalyst bed is 18 micrometers in mean particle diameter.

[0037] Next, the fuel cell of the structure shown in drawing 1 of the example 1 of an operation gestalt is assembled using the air electrode concerning each above-mentioned samples 1 and 2 and the comparison sample C1. The hydrogen electrode in the above-mentioned fuel cell consists of a gaseous diffusion layer and a catalyst bed, and this catalyst bed consists of carbon black, PTFE, cation exchange resin, and platinum. And the thickness of this gaseous diffusion layer is 180 micrometers, and the thickness of a catalyst bed is 20 micrometers.

[0038] And pure hydrogen is supplied to the above-mentioned hydrogen electrode. Moreover, the air incorporated from the open air in the air compressor is supplied to the above-mentioned air electrode. Moreover, the above-mentioned solid electrolyte consists of cation-exchange-resin film, and is 60 micrometers in thickness.

[0039] Thus, it is attached to the constituted fuel cell and is 0.5 A/cm<sup>2</sup>. The electrical potential difference when changing the relation between the electrical potential differences and air utilization rates in the condition of having passed the current, by unit 10% to 10% - 50% of air utilization rates in the condition of having given the fixed load and having held to the constant current of 0.5 A/cm<sup>2</sup> was measured. At this time, a hydrogen utilization factor is 80% and gas pressure is operating hydrogen and air by ordinary pressure. In addition, as for the fuel cell under measurement, the temperature of each electrode was held at 80 degrees C. It is shown in drawing 5 about the above-mentioned result.

[0040] It is a ratio between the number of oxygen molecules with which the air utilization rate was consumed here in number [ of the oxygen molecules in the air supplied to the air electrode per unit time amount ], cell reaction [ of a fuel cell ], and  $H_2 + (1/2) O_2 \rightarrow H_2 O$ . Since measurement concerning this example is performed by current regularity, the air utilization rate concerning this example is proportional to the number of the oxygen molecules in the air supplied to the air electrode.

[0041] That is, the currents which all the oxygen molecules in the supplied air were consumed by the cell reaction, and were acquired by this cell reaction are 0.5 A/cm<sup>2</sup> in 100% of air utilization rates. The condition of having become is shown. And in measurement of this example, that an air utilization rate decreases shows that the amount of supply of air increased. Therefore, it can be said that a current can be taken out from a fuel cell by the small air content, so that an air utilization rate is high. And the fuel cell is wanted to operate in the part from which an air utilization rate generally becomes 40% or more.

[0042] As shown in drawing 5, when the air utilization rate exceeded 40%, the electrical potential difference of the fuel cell which used the comparison sample C1 fell greatly. Even if, as for the sample 1 and sample 2 concerning this example, the air utilization rate exceeded 40%, an electrical potential difference did not fall so much. The above showed that the fuel cell using the air electrode concerning this invention could maintain high performance also in the condition that an air utilization rate is high. Therefore, power with the air sufficient at least to which the fuel cell concerning this invention is supplied could be taken out, and it turned out that air can be used effectively.

[0043]

[Effect of the Invention] According to this invention, like the above, the air electrode for fuel cells which can raise an air utilization rate, and its manufacture approach can be offered.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The explanatory view about the structure of a fuel cell in the example 1 of an operation gestalt.

[Drawing 2] The important section expansion explanatory view of the catalyst bed in a hydrogen electrode in the example 1 of an operation gestalt.

[Drawing 3] The explanatory view showing the chemical structure type of the vanadium oxide of a co-catalyst in the example 1 of an operation gestalt.

[Drawing 4] The explanatory view showing the chemical structure type of the Seria zirconia complex of a co-catalyst in the example 2 of an operation gestalt.

[Drawing 5] The explanatory view showing the relation of the electrical potential difference of a fuel cell and air utilization rate concerning the sample and comparison sample in the example 3 of an operation gestalt.

[Description of Notations]

- 1 ... a fuel cell,
- 11 ... a hydrogen electrode,
- 14 ... a gaseous diffusion layer,
- 15 ... a catalyst bed,
- 160 ... a conductive particle,
- 161 ... a main catalyst,
- 162 ... a co-catalyst,

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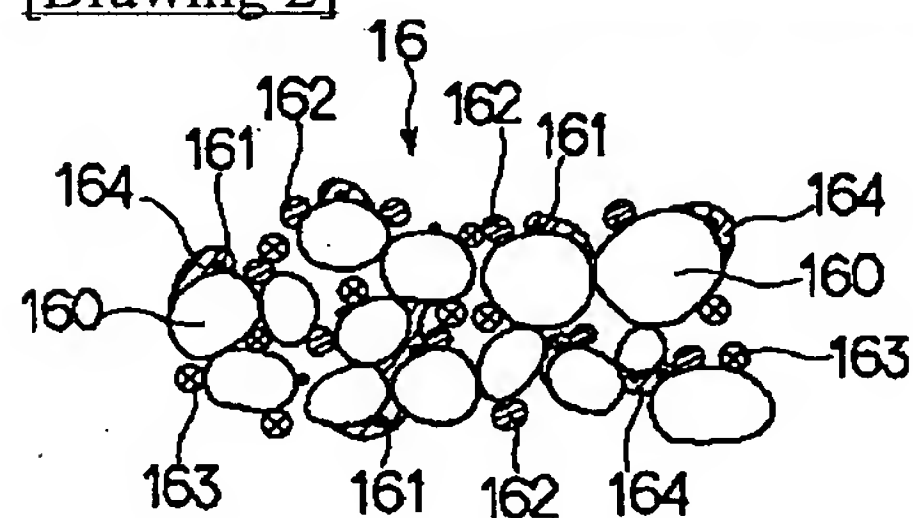
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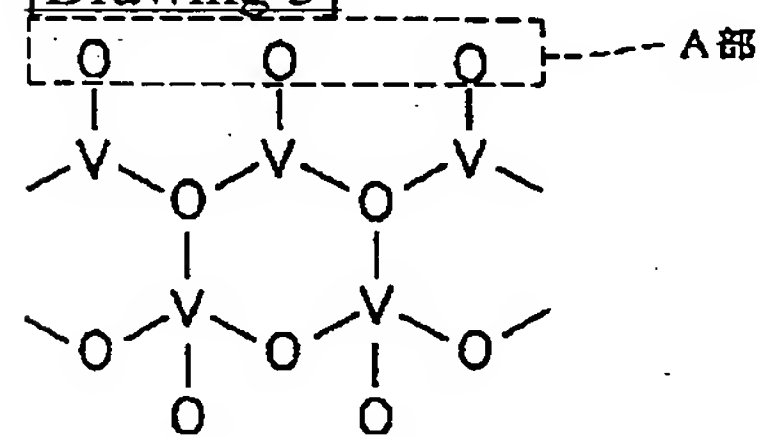
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## DRAWINGS

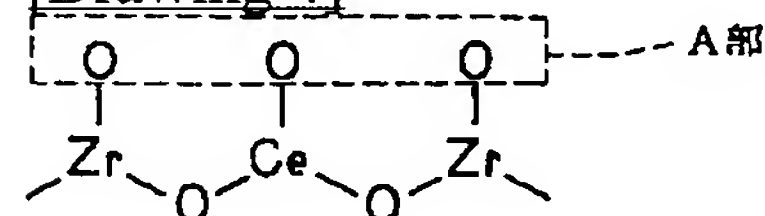
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Drawing 1]





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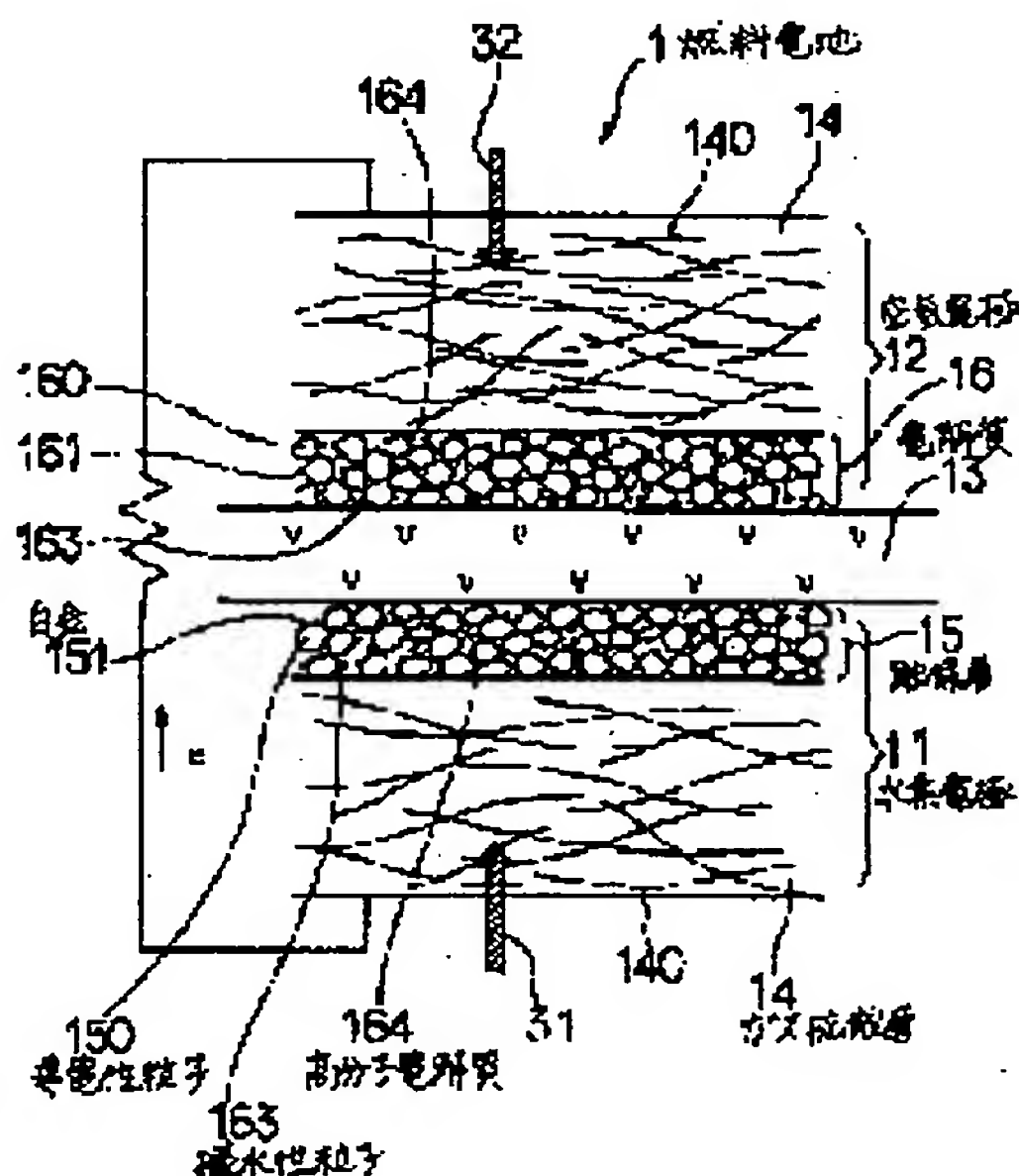
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**PROBLEM TO BE SOLVED:** To improve the air utilization factor by forming an electrode of a gas diffused layer and catalyst layers formed on the surface of the gas diffused layer, and forming the catalyst layer of conductive grains, water repellent grains, high molecular electrolyte, main catalyst and auxiliary catalyst.

**SOLUTION:** A hydrogen electrode 11 and an air electrode 12 of a fuel cell 1 are respectively formed of a gas diffused layer 14 and catalyst layers 15, 16 formed on the surface of the gas diffused layer. The catalyst layer 16 of the air electrode 12 is formed of carbon black as conductive grains 160, PTFE as water repellent grains 163, positive ion exchange resin as high molecular electrolyte 164, granular platinum as main catalyst 161 and vanadium oxide as auxiliary catalyst 162. The catalyst layer 15 of the hydrogen electrode 11 is formed of carbon black as conductive grains 160, granular platinum carried by the carbon black, PTFE as water repellent grains 163 and positive ion exchange resin as high molecular electrolyte 164. The gas diffused layer 14 of the electrodes 11, 12 is formed of a carbon fiber plate formed by laminating carbon fibers 140.



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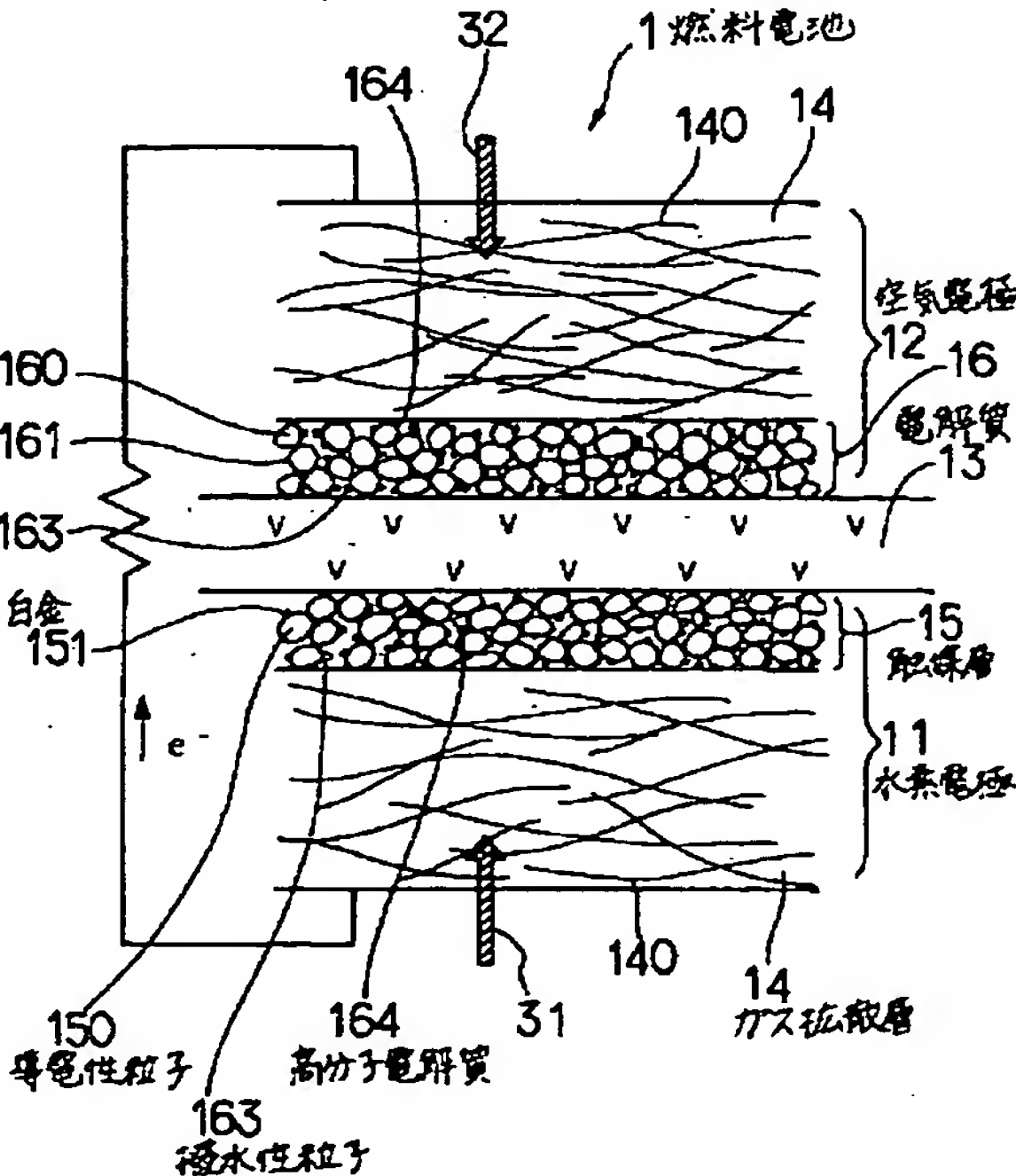
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(54)【発明の名称】 燃料電池用空気電極及びその製造方法

(57)【要約】  
【課題】 空気利用率を高めることができる、燃料電池用空気電極及びその製造方法を提供すること。  
【解決手段】 ガス拡散層14とその表面に形成した触媒層16とよりなる。上記触媒層16は、導電性粒子160、撥水性粒子163、高分子電解質164、主触媒161、助触媒162よりなり、該助触媒は酸化バナジウム、酸化セリウム、酸化ジルコニウムまたはこれらの物質の2種以上の複合体とよりなる。





## 【特許請求の範囲】

【請求項1】 ガス拡散層とその表面に形成した触媒層とよりなる燃料電池用空気電極であって、上記触媒層は、導電性粒子、撥水性粒子、高分子電解質、主触媒及び助触媒よりなり、該助触媒は、酸化バナジウム、酸化セリウム、酸化ジルコニウムまたはこれらの物質の2種以上の複合体よりなることを特徴とする燃料電池用空気電極。

【請求項2】 ガス拡散層とその表面に形成した触媒層とよりなり、該触媒層は、導電性粒子、撥水性粒子、高分子電解質、主触媒及び助触媒よりなり、また、該助触媒は、酸化バナジウム、酸化セリウム、酸化ジルコニウムまたはこれらの物質の2種以上の複合体よりなる燃料電池用空気電極を製造するに当たり、上記触媒層を構成する導電性粒子層に白金を担持し、次いで該導電性粒子層をバナジウム、セリウム、ジルコニウムの少なくとも1つを含有する溶液中に浸漬、乾燥し、その後加熱することを特徴とする燃料電池用空気電極の製造方法。

## 【発明の詳細な説明】

## 【0001】

【技術分野】本発明は、水素電極と空気電極と両者の間に配置された電解質とよりなる燃料電池の空気電極及びその製造方法に関する。

## 【0002】

【従来技術】従来、後述の図1に示すごとく、水素電極11と空気電極12と両者の間に配置された電解質13とよりなり、水素及び酸素を電極活物質として使用する燃料電池1が知られている。上記燃料電池1において、水素電極11及び空気電極12は共にガス拡散層14とその表面に形成した触媒層15、16とよりなり、該触媒層15、16は導電性粒子150、160であるカーボンブラックと、これに担持された白金粒子151、161、撥水性粒子163、高分子電解質164とよりなる。

【0003】上記燃料電池における起電力の発生は以下に示すごとく行なわれる。上記水素電極に水素含有ガスが、空気電極に酸素含有ガスとしての空気が外部より供給される。これにより水素電極にて $H_2 \rightarrow 2H^+ + 2e^-$ 、空気電極にて $(1/2)O_2 + 2e^- + 2H^+ \rightarrow H_2O$ という電極反応が発生する。従って、 $H_2 + (1/2)O_2 \rightarrow H_2O$ という電池反応が発生し、これにより燃料電池が起電する。そして、この電極反応における触媒作用を上記触媒層に存在する白金粒子が担っている。

## 【0004】

【解決しようとする課題】ところで、上記構造の燃料電池における電池性能は、空気電極の分極特性により支配されており、従って空気電極の側の触媒層の特性の向上が電池性能の向上に効果的である。

【0005】即ち、上記従来の燃料電池は、空気電極に供給された空気利用率が低く、従って、電池性能の向上

のためには空気量を多くする必要があった。この問題に対する改善策としては、例えば、空気を燃料電池に送り込むために使用するコンプレッサーを大型のものとすることが考えられる。しかしながら、上記燃料電池を、例えば電気自動車等、設置スペースの限られた状態において使用する場合には、大型のコンプレッサーを使用することは困難である。従って、空気利用率を高め、少量の空気でも十分な電圧を得られる燃料電池が要求されている。

10 【0006】本発明は、かかる問題点に鑑み、空気利用率を高めることができる、燃料電池用空気電極及びその製造方法を提供しようとするものである。

## 【0007】

【課題の解決手段】請求項1の発明は、ガス拡散層とその表面に形成した触媒層とよりなる燃料電池用空気電極であって、上記触媒層は、導電性粒子、撥水性粒子、高分子電解質、主触媒及び助触媒よりなり、該助触媒は、酸化バナジウム、酸化セリウム、酸化ジルコニウムまたはこれらの物質の2種以上の複合体よりなることを特徴とする燃料電池用空気電極にある。

20 【0008】上記燃料電池用空気電極を設ける燃料電池としては、例えば、後述の図1に示すごとく、水素電極と空気電極と両者の間に配置された電解質とよりなり、水素及び酸素を電極活物質として使用する燃料電池を挙げることができる。上記空気電極に対しては外部よりガス拡散層を通じて空気を供給することができ、これに含まれる酸素を消費して前述した電極反応が発生する。なお、上記空気の供給は、例えばエアコンプレッサーを利用し、外気をそのまま空気電極に対し送り込むことにより行うことができる。

30 【0009】また、上記ガス拡散層としては、例えば、カーボンファイバーを集積、成形した炭素繊維板を使用することができる。上記導電性粒子としては、カーボンブラック、上記撥水性粒子としては、例えば、ポリテトラフルオロエチレン（以降PTFEと省略）、上記高分子電解質としては、例えば、陽イオン交換樹脂を使用することができる。

40 【0010】上記主触媒は、上記空気電極において電極反応を促進する役割を有しており、例えば、白金を使用することができる。また、上記触媒層における助触媒の担持量は、 $0.1 \sim 2.0 \text{ mg/cm}^2$ とすることが好ましい。上記助触媒の担持量が $2.0 \text{ mg/cm}^2$ より多い場合には、逆にガス通路を防ぐような構造となり、更に電気抵抗を増大させ、特性の低下を招くおそれがある。一方、 $0.1 \text{ mg/cm}^2$ 未満である場合には、助触媒としての機能が十分に働かないおそれがある。なお、上記助触媒の担持量の単位「 $\text{mg/cm}^2$ 」は、電極の単位面積当たりに担持された助触媒の重量を意味する。

50 【0011】また、上記触媒層における撥水性粒子の担

持量は、導電性粒子：撥水性粒子＝8：2～6：4（重量比）とすることが好ましい。上記撥水性粒子の担持量が8：2未満である場合には、撥水性が弱いおそれがある。一方、6：4より多い場合には、電気抵抗が大きくなるおそれがある。なお、最も好ましい上記撥水性粒子の担持量は、導電性粒子：撥水性粒子＝7：3（重量比）である。

【0012】また、上記触媒層における高分子電解質の担持量は0.08～2mg/cm<sup>2</sup>とすることが好ましい。上記高分子電解質の担持量が0.08mg/cm<sup>2</sup>未満である場合には、電極反応が遅くなるおそれがある。一方、2mg/cm<sup>2</sup>より多い場合には、電気抵抗が大きくなるおそれがある。なお、上記高分子電解質の担持量は乾燥重量、単位は上記助触媒の場合と同様である。

【0013】本発明の作用につき、以下に説明する。本発明にかかる触媒層においては、助触媒として酸化バナジウム、酸化セリウム、酸化ジルコニウムまたはこれらの物質の2種以上の複合体が担持してある。これらの物質はバナジウム、セリウム、ジルコニウム1原子に対して結合する酸素原子の個数が不定である酸化物である。そして、上記物質は、後述する図3、図4に示すとき鎖状の構造を有し、かつ、特定の部分に結合した酸素原子が比較的自由に出入り可能となっている（同図において点線にて囲ったA部にかかる酸素原子が該当する）。

【0014】そのため、上記物質は、周囲の雰囲気酸素リッチとなれば、酸素原子を放出することができ、一方周囲の雰囲気酸素リッチとなれば、酸素原子を吸収することができる。よって、上記触媒層付近において、常に酸素を一定以上の濃度に保持することができる。従って、空気電極において過電圧を低く抑えることができ、空気利用率を高めることができる。また、一時的に空気の供給が不足した場合には、上記助触媒より酸素が放出されるため、この放出酸素を利用して空気電極は電極反応を継続することができる。

【0015】以上のように、本発明によれば、空気利用率を高めることができる。燃料電池用空気電極を提供することができる。

【0016】次に、請求項2の発明は、ガス拡散層とその表面に形成した触媒層とよりなり、該触媒層は、導電性粒子、撥水性粒子、高分子電解質、主触媒及び助触媒よりなり、また、該助触媒は、酸化バナジウム、酸化セリウム、酸化ジルコニウムまたはこれらの物質の2種以上の複合体よりなる燃料電池用空気電極を製造するに当たり、上記触媒層を構成する導電性粒子層に白金を担持し、次いで該導電性粒子層をバナジウム、セリウム、ジルコニウムの少なくとも1つを含有する溶液中に浸漬、乾燥し、その後加熱することを特徴とする燃料電池用空気電極の製造方法にある。

【0017】これにより、主触媒として白金を用いた空

気電極であり、請求項1に示した、燃料電池における空気利用率を高めることができる燃料電池用空気電極を得ることができる。また、上記製造方法においては導電性粒子に対し、主触媒となる白金を先に担持、また助触媒の担持に際しては、熱処理温度350℃以下という条件にて行うことが好ましい。これにより、白金の凝集を防止することができる。

【0018】また、上記バナジウム、セリウム、ジルコニウムの少なくとも1つを含有する溶液としては、例えば、過塩素酸バナジウムのエタノール溶液、硝酸セリウムのエタノール溶液、硝酸ジルコニルのエタノール溶液等を挙げることができる。

【0019】

【発明の実施の形態】

実施形態例1

本発明の実施形態例にかかる燃料電池用空気電極及びこの電極を設けた燃料電池につき、図1、図2を用いて説明する。図1、図2に示すごとく、本例の燃料電池用空気電極12は、ガス拡散層14とその表面に形成した触媒層16とよりなり、上記触媒層16は導電性粒子160、撥水性粒子163、高分子電解質164、主触媒161、助触媒162よりなり、該助触媒162は酸化バナジウムよりなる。

【0020】まず、本例にかかる燃料電池1につき説明する。図1に示すごとく、上記燃料電池1は、水素電極11と空気電極12と両者の間に配置された固体電解質13とよりなり、水素及び酸素を電極活物質として使用する燃料電池である。上記燃料電池1において、水素電極11及び空気電極12は共にガス拡散層14とその表面に形成した触媒層15、16とよりなる。

【0021】そして、上記空気電極12の触媒層16は、導電性粒子160であるカーボンブラック、撥水性粒子163であるPTFE、高分子電解質164である陽イオン交換樹脂、上記カーボンブラックの表面に担持された主触媒161である粒子状の白金及び助触媒162である酸化バナジウムとよりなる。また、上記水素電極11の触媒層15は導電性粒子150であるカーボンブラックと、これに担持された粒子状の白金151、撥水性粒子163であるPTFE、高分子電解質164である陽イオン交換樹脂とよりなる。

【0022】また、上記水素電極11、空気電極12におけるガス拡散層14はカーボンファイバー140を集積、成形した炭素繊維板よりなる。なお、上記水素電極11における白金151の触媒層15への担持量は0.2mg/cm<sup>2</sup>である。一方、上記空気電極12における白金161の触媒層16への担持量は0.2mg/cm<sup>2</sup>である。

【0023】また、上記水素電極11及び上記空気電極12において共に、上記撥水性粒子163の担持量は、導電性粒子：撥水性粒子＝7：3（重量比）、上記陽イ



オン交換樹脂164の担持量は、 $0.4\text{ mg/cm}^2$ である。

【0024】そして、上記水素電極11には水素含有ガス31が、空気電極12には空気32が供給される。これらの水素含有ガス31、空気32はそれぞれの電極におけるガス拡散層14側より導入する。更に、上記水素電極11と空気電極12との間には、陽イオン交換樹脂膜よりなる固体電解質13が配置されている。

【0025】本例の助触媒である酸化バナジウムにつき説明する。上記酸化バナジウムは、図3に示すとき鎖状の構造を有している。そして、同図において点線にて囲ったA部にかかる酸素原子が外部の酸素濃度に応じて出入りする。

【0026】次に、上記空気電極12の製造方法につき説明する。まず、上記ガス拡散層14に対し、カーボンブラック及びPTFEの混合粉をバインダを含む溶剤と混練することによりペースト状にし、上記ガス拡散層14の上にドクターブレードを用いて、シート状に成形する。

【0027】次に、上記付着したカーボンブラックに対し、 $\text{Pt}(\text{NO}_3)(\text{NH}_3)_2$  硝酸溶液を含浸、乾燥後に温度 $180\sim 300^\circ\text{C}$ 、水素ガス雰囲気（水素還元雰囲気）にて熱処理を行う。以上により、上記カーボンブラックの表面に粒子状の白金が析出する。次に、上記カーボンブラックに対し、過塩素酸バナジウム（ $\text{VC1}$ 、 $\text{O}$ ）のエタノール溶液を含浸、乾燥させる。その後、温度 $350^\circ\text{C}$ 、空気中にて熱処理を行う。更に、上記触媒層16に、陽イオン交換樹脂溶液を含浸、乾燥させる。以上により、空気電極12を得た。

【0028】次に、本例における作用効果につき説明する。本例の空気電極12の触媒層16においては、助触媒162として、図3に示すとき、酸化バナジウムが担持してある。上記酸化バナジウムは、周囲の雰囲気が酸素リッチとなれば、酸素原子を放出することができ、一方周囲の雰囲気が酸素リッチとなれば、酸素原子を吸収することができる。よって、上記触媒層16付近において、常に酸素の濃度を一定以上に保持することができる。

【0029】従って、空気電極12において過電圧を低く抑えることができ、空気利用率を高めることができる。また、一時的に空気の供給が不足した場合には、上記助触媒162より酸素が放出されるため、この放出酸素を利用して空気電極12は電極反応を継続することができる。

【0030】以上のように、本例によれば、空気利用率を高めることができる、燃料電池用空気電極を提供することができる。

#### 【0031】実施形態例2

本例は、図4に示すごとく、助触媒としてセリア・ジルコニアを使用した空気電極である。本例にかかる空気電

極は、実施形態例1と同様に、ガス拡散層とその表面に形成した触媒層とよりなり、上記触媒層は導電性粒子であるカーボンブラック、撥水性粒子のPTFE、高分子電解質の陽イオン交換樹脂、主触媒の白金と助触媒とよりなる。

【0032】そして、図4に示すごとく、上記助触媒は鎖状の構造を有するセリア・ジルコニア複合体よりなり、同図において点線にて囲ったA部にかかる酸素原子が外部の酸素濃度に応じて出入りする。また、上記セリア・ジルコニア複合体の化学式は $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ （ $x=0.4\sim 0.7$ ）で表される。その他は、実施形態例1と同様である。

【0033】次に、本例の空気電極の製造方法につき説明する。実施形態例1と同様にカーボンファイバーよりなるガス拡散層に、カーボンブラック及びPTFEの混合粉を付着させる。次いで、上記カーボンブラックに対し白金を担持させる。

【0034】次に、上記カーボンブラックに対し、硝酸セリウム（ $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ）のエタノール溶液、硝酸ジルコニル（ $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ）のエタノール溶液を含浸、乾燥させる。その後、温度 $350^\circ\text{C}$ 、空気中にて熱処理を行う。更に、上記触媒層に、陽イオン交換樹脂溶液を含浸、乾燥させる。以上により、空気電極を得た。なお、本例の空気電極においても実施形態例1と同様の作用効果を有する。

#### 【0035】実施形態例3

本例は、本発明にかかる空気電極の性能を、試料1、試料2と共に比較試料C1を用いて、説明するものである。試料1は実施形態例1に示した空気電極である。試料2は実施形態例2に示した空気電極である。比較試料C1は、助触媒を含有していないことを除いて、上述の試料1及び2と同様の空気電極である。

【0036】なお、上記試料1、2、比較試料C1のいずれの空気電極におけるガス拡散層も厚さが $180\mu\text{m}$ であり、触媒層の厚さは $20\mu\text{m}$ である。そして、上記触媒層にかかるカーボンブラックは平均粒径 $18\mu\text{m}$ である。

【0037】次に、上記各試料1、2及び比較試料C1にかかる空気電極を用いて、実施形態例1の図1に示した構造の燃料電池を組み立てる。上記燃料電池における水素電極はガス拡散層と触媒層とよりなり、この触媒層はカーボンブラック、PTFE、陽イオン交換樹脂、白金よりなる。そして、このガス拡散層の厚さは $180\mu\text{m}$ であり、触媒層の厚さは $20\mu\text{m}$ である。

【0038】そして、上記水素電極に対して純水素を供給する。また、上記空気電極にはエアコンプレッサーにて外気より取込まれた空気が供給されている。また、上記固体電解質は陽イオン交換樹脂膜よりなり、厚さ $60\mu\text{m}$ である。

【0039】このように構成した燃料電池につき、0.



5 A/cm<sup>2</sup> の電流を流した状態における電圧と空気利用率との間の関係を、一定負荷を与えて、0.5 A/cm<sup>2</sup> の定電流に保持した状態で空気利用率10%~50%まで、10%きざみで変化させた時の電圧を測定した。この時、水素利用率は80%で、ガス圧力は水素、空気共に常圧で運転している。なお、測定中の燃料電池は各電極の温度が80℃に保持されていた。上記結果につき、図5に示す。

【0040】ここに、空気利用率とは、単位時間あたり空気電極に対し供給された空気中の酸素分子の数と、燃料電池の電池反応、 $H_2 + (1/2) O_2 \rightarrow H_2 O$ において消費された酸素分子の数との間の比である。本例にかかる測定は電流一定で行っているため、本例にかかる空気利用率は、空気電極に対し供給された空気中の酸素分子の数と比例する。

【0041】即ち、空気利用率100%とは、供給された空気中の酸素分子全てが電池反応に消費され、該電池反応により得られた電流が0.5 A/cm<sup>2</sup> となった状態を示している。そして、本例の測定において、空気利用率が減少することは、空気の供給量が多くなったことを示している。従って、空気利用率が高いほど、少ない空気量で燃料電池より電流を取出すことができるといえる。そして、一般的には空気利用率が40%以上となる部分で燃料電池が作動することが望まれている。

【0042】図5に示すごとく、空気利用率が40%を越えた時点で、比較試料C1を使用した燃料電池の電圧は大きく低下した。本例にかかる試料1、試料2は空気利用率が40%を越えても、さほど電圧が低下しなかった。以上により、本発明にかかる空気電極を用いた燃料\*

\*電池は、空気利用率が高い状態でも、高性能を維持できることが分かった。従って、本発明にかかる燃料電池は供給される空気が少なくとも、十分な電力を取出すことができ、空気を有効に利用できることが分かった。

【0043】

【発明の効果】上記のごとく、本発明によれば、空気利用率を高めることができる、燃料電池用空気電極及びその製造方法を提供することができる。

【図面の簡単な説明】

10 【図1】実施形態例1における、燃料電池の構造についての説明図。

【図2】実施形態例1における、水素電極における触媒層の要部拡大説明図。

【図3】実施形態例1における、助触媒の酸化バナジウムの化学構造式を示す説明図。

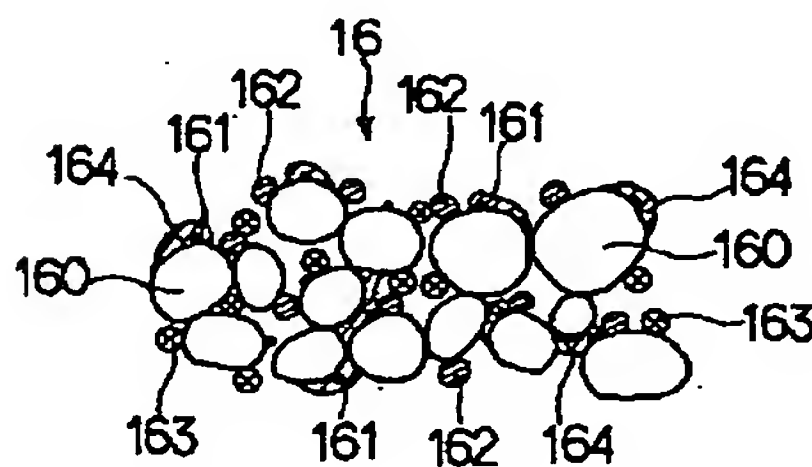
【図4】実施形態例2における、助触媒のセリア・ジルコニア複合体の化学構造式を示す説明図。

20 【図5】実施形態例3における、試料及び比較試料にかかる燃料電池の電圧と空気利用率との関係を示す説明図。

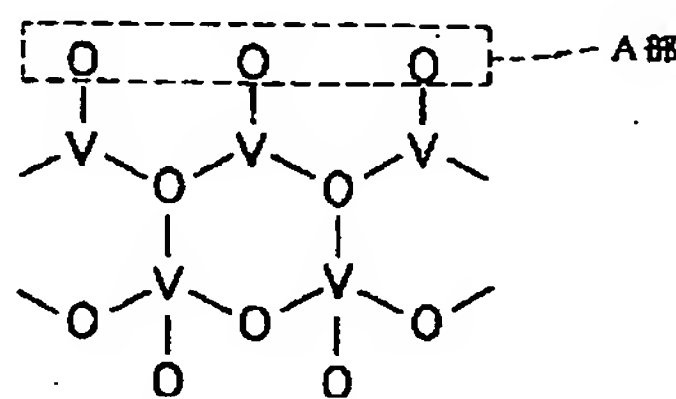
【符号の説明】

- 1... 燃料電池,
- 11... 水素電極,
- 14... ガス拡散層,
- 15... 触媒層,
- 160... 導電性粒子,
- 161... 主触媒,
- 162... 助触媒,

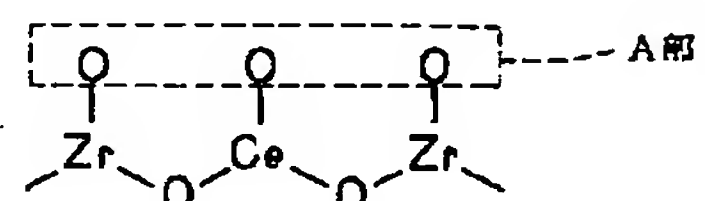
【図2】



【図3】



【図4】



【图 5】

